EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

Experiment title:	Experiment number:
Ferric iron in silicate glass from silicate/alloy equilibration experiments at 30-80 GPa: the redox processes during terrestrial planet/exoplanet differentiation	ES-1330

Beamline:	Date of experiment:	Date of report:
ID18	from: 31.01.2023 to: 06.02.2023	16.08.2023
Shifts: 18	**Local contact(s):** Sergey Yaroslavtsev	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Hongluo Zhang[1]*, Marc M Hirschmann[2]*, Michael J Walter[3], Oliver T Lord[4], Anja Rosenthal[5,6]*, Sergey Yaroslavtsev[5], Alexander I Chumakov[5], Elizabeth Cottrell[7]*

[1]*China University of Geosciences, State Key Laboratory of Geol. Processes & Mineral Res., Beijing, China,*
[2]*University of Minnesota Twin Cities, Department of Earth & Environmental Sciences, Minneapolis, U.S.,*
[3]*Carnegie Institution for Science, Earth and Planets Laboratory, Washington, United States,*
[4]*University of Bristol, School of Earth Sciences, Bristol, United Kingdom,*
[5]*ESRF European Synchrotron Radiation Facility, Grenoble, France,*
[6]*The Australian National University, Research School of Earth Sciences, Canberra, Australia,*
[7]*Smithsonian, NMNH, Department of Mineral Sciences, Washington, DC, U.S.*

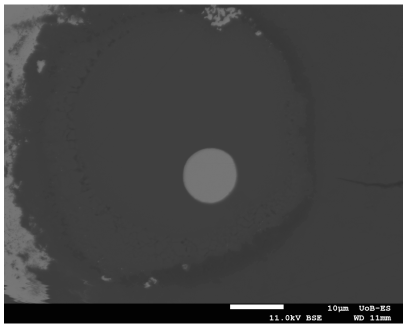
Report: This study examines the stability of Fe_2O_3 in deep magma oceans during early evolution of rocky planets. The greater the stability of Fe_2O_3 in silicate melts reacting with core-destined molten Fe alloy, the more oxidized planetary surface conditions will be, affecting planetary evolution and habitability. The redox-depth profile of a convecting magma ocean (MO) has been explored previously through theoretical and experimental studies[1-7]. Both experiments and first principles (FPMD) calculations affirm that a deep terrestrial MO, alloy-saturated at its base, becomes enriched in Fe^{3+}, leading to relatively oxidized near-surface conditions[3,4,6]. But previous experiments[2,3,7] are limited to ≤ 28 GPa and ≤ 3000 K and at high pressures (P), experiments and FPMD calculations conflict; e.g., at 30 GPa, extrapolation of the former suggest MO Fe^{3+}/Fe^{T} of ≥0.35[3,7] whereas FPMD suggest 0.04-0.07[4].

We used energy-domain synchrotron Mössbauer spectroscopy (SMS) at ID18, ESRF to measure $Fe^{3+}/\Sigma Fe$ ratios and Fe-bonding environments in quenched silicate glasses recovered from laser-heated diamond anvil (LH-DAC) experiments in which mafic melts were equilibrated with PtFe alloys. These were used to calibrate a thermodynamic model relating Fe^{3+}/Fe^{T} ratios to magma ocean depth and applied to early evolution of rocky planets. Also, to gauge the effects of different fitting strategies on the accuracy of the SMS analyses, we analyzed a suite of mafic glasses which had previously been analyzed by conventional Mössbauer spectroscopy[2].

Sample details: We achieved successful analyses of 9 silicate-alloy equilibration experiments performed with LH-DAC from 38 GPa to 71 GPa and 3800-4400 K and ΔIW from -0.4 to +0.8. All had produced well-segregated alloy and silicate domains, with no disseminated alloy detected in the silicate (Fig. 1). Major and minor compositions of the quenched glasses and alloys were obtained by using the electron microprobe.

SMS measurements: The Fe^{3+}/Fe^{T} ratios of quenched glasses were quantified by SMS collected at ID18 (Fig. 2). Using secondary standards (Figs. 2a, 2b), we tested multiple different fitting strategies and software implementations, but ultimately concluded that the best results were obtained using the Gaussian ratio method

Figure 1: BSE image of experiment DAC93, (43.41, 3802±93 K, ΔIW=0.46), showing concentric structure with FePt alloy ball surrounded by homogeneous quenched silicate glass.



implemented in the new SYNCmoss software package[8]. In addition to analyses of glass only (Figs. 2c, 2e), we also measured areas in which both glass and alloy or glass and neighboring perovskite (Figs. 2d, 2f) were included in the incident beam. These allowed us to distinguish the characteristics of analyses that were not purely glass, and helped assure that the accepted analyses from each experiment were those of quenched melt only.

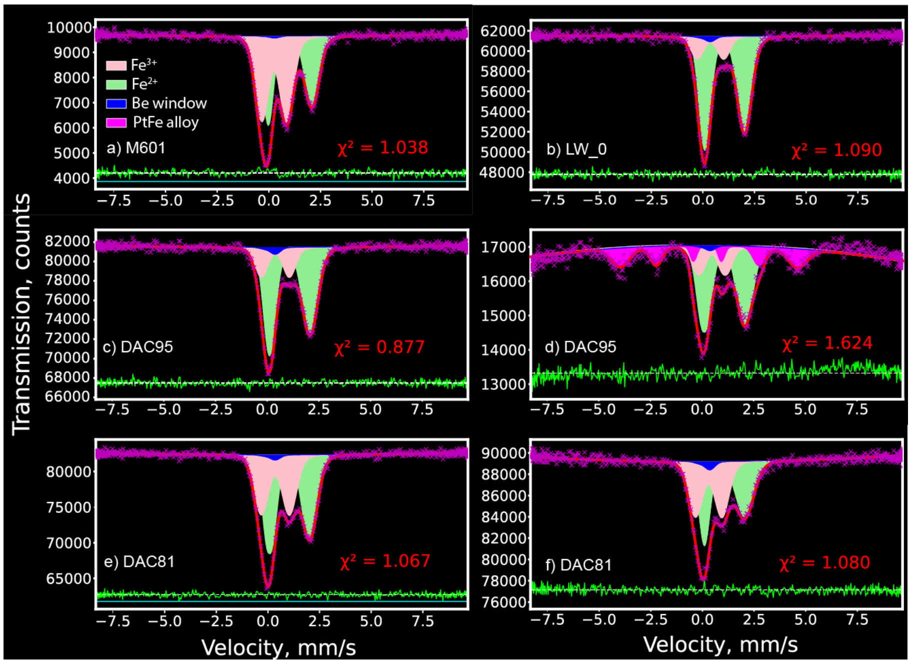


***Fig. 2** Examples of E-SMS spectra from secondary standards (a) M601 and (b) LW_0, from (c) pure heated glass quenched from LH-DAC experiment (exp) DAC95, (d) glass from exp DAC95 contaminated with PtFe alloy e) pure heated glass from exp DAC81; f) glass area contaminated with Ca-perovskite from exp DAC81. The blue asymmetric doublets are from the Be lens, the pink symmetric doublets represent ferric paramagnetic sites, and the light green asymmetric doublets indicate ferrous paramagnetic sites. The X^2 values are close to 1 for all spectra, except for the deliberately PtFe-contaminated sample, suggesting the robustness of our fitting approach. The accurate determination of the heated glass region is achieved through the co-location of optical measurements and X-ray scans. The presence of a sextet in the Mossbauer spectra, (panel d), can indicate alloy contamination, though this phenomenon is not observed across all our E-SMS of DAC experimental samples.*

Results: SMS spectra of glasses consist of two broadened doublets derived from paramagnetic Fe^{2+} and Fe^{3+}. Resolved hyperfine parameters, center shift (CS) and quadrupole splitting (QS) are greater than those evident in similar glasses quenched from lower pressure[2], and resulting Fe^{3+}/Fe^T ratios range from 0.20 to 0.45, diminishing with increasing pressure. When adjusted for differences in melt composition, oxygen fugacity (fO_2), and temperature (T), the new results are similar to the predictions from first principals calculations[4], but melts have significantly less Fe^{3+} than implied by exptrapolation of the lower pressure experimental studies[3,7]. We used the new results obtained by SMS to update a recent thermodynamic model for silicate melt Fe^{3+}/Fe^T as a function of *T*, *P*, composition, and fO_2[6], by adjusting the parameters in a Birch-Murnaghan EOS. Applying this model along hot and cold magma ocean (MO) geotherm paths[9] at ΔIW-2 (Fig 3), the oxygen fugacity appropriate for the MO during core formation and equilibration with Fe-rich alloy, we find that Fe^{3+}/Fe^T reaches ~0.12 at 33 GPa and maintains approximately the same value to 80 GPa along the hot geotherm, and for the cold geotherm, the Fe^{3+}/Fe^T reaches maximum of 0.084 at 34 GPa and thereafter diminishes gradually (0.06 at 80 GPa). Therefore, depending on the conditions of silicate-alloy equilibration, the atmosphere above a terrestrial MO may have been comparatively oxidized, and nearly all of the Fe_2O_3 present in the modern mantle may have originated in the MO, without additions from bridgmanite disproportionation or hydrogen escape.

Results will be presented at AGU23 in December 2023 and will also be submitted for publication. Because these results will have wide impact across disciplines (earth, planetary, and astrophysical sciences), we anticipate publication in a high profile (Nature/Science/PNAS) family journal.

References: **[1]** Hirschmann, M.M. (2012) EPSL **[2]** Zhang et al. (2017) GCA **[3]** Armstrong et al. (2019) Science **[4]** Deng et al. (2020) Nature Comm. **[5]** Sossi et al. [2020] Science **[6]** Hirschmann (2022) GCA **[7]** Kuwahara et al. (2023) Nature Geoscience **[8]** Yaroslavtsev et al. (2023) J Synchrotron Rad.